A Review of Different Forms of Sulfate Attack

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Types of Sulfate Standards

1. Cementitious Materials Standard Tests (ASTM, CSA)

- Excess internal sulfate
- Chemical resistance to external sulfate attack

2. Concrete Codes (ACI, CSA)

- Concrete Standards (ACI, CSA)
- For external sulfate resistance
- Based on degree of exposure
- Control concrete quality (w/c) as well as materials
- TSA: not mentioned
- DEF: Mentioned indirectly through controls on maximum early temperature (CSA A23.4, and possibly coming to ACI C308)

Internal Sulfate Attack

- ISA can occur if there are excess sulfates from constituent materials which can dissolve into the pore solution in service conditions.
  - Eg. excess SO3 in cement or fly ash
  - Eg. Heat treatment > 70C which upsets the normal formation of ettringite in the first hours of hydration, which in some cases can cause DEF.

In the DOE case…

- I understand that the sulfates in the cemented wastes are in the form of ppt’d sulfate salts.
- The concern is that if moisture enters the waste form in the future, sulfates will become soluble could result in ISA.

Forms of Sulfate Attack

- While the threat of ettringite formation maybe addressed by limiting sources of reactive alumina, other forms of sulfate attack exist.
- Salt crystallization: if soluble sulfates migrate then re-ppte. then could get expansive pressures---perhaps not likely here.
- Thaumasite: A calcium- carbonate- silicate- hydrate which attacks the C-S-H matrix and causes softening and loss of integrity of the concrete.

External Sulfate Attack

Bridge columns in North Dakota in sulfate soils

Sulfate Resistant Cements

- In 1919, Thorbergur Thorvaldson, at the University of Saskatchewan, initiated studies and in 1927 reported that C_3A was responsible for the deterioration of cements exposed to sulfate solutions, and later that high iron cements were more resistant (In 1928, Hansen, Brownmiller, and Bogue identified this phase as C_4AF).
- The Canada Cement Co.,who had funded the research, then patented the first Type V sulfate resistant cement, Kalicrete, in 1933.

Concrete: Effect of C_3A in Portland Cement
w/c =0.50, 21 years in 50,000 ppm $MgSO_4$

12.3 % C_3A **7.1 % C_3A** **3.5 % C_3A**

(Saw Cut cylinders on right side)

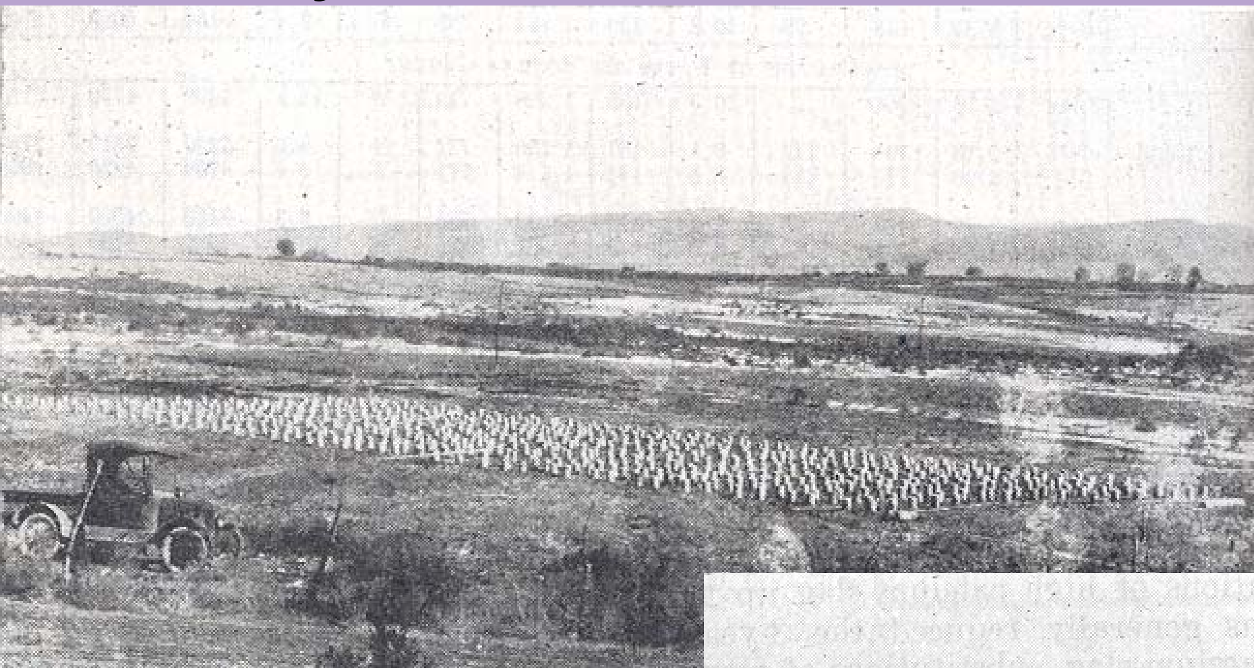
Brown, Hooton and Clark,

On T. Thorvaldson’s work , 1928

- “Of special significance, then as now, was the finding that a concentration of soil or soil-water alkalis (ie. sulfates) was not always a measure of the degree of deterioration to be expected, but that capillary action and subsequent evaporation were major factors.”

E.G. Swenson and C.J. Mackenzie, 1968

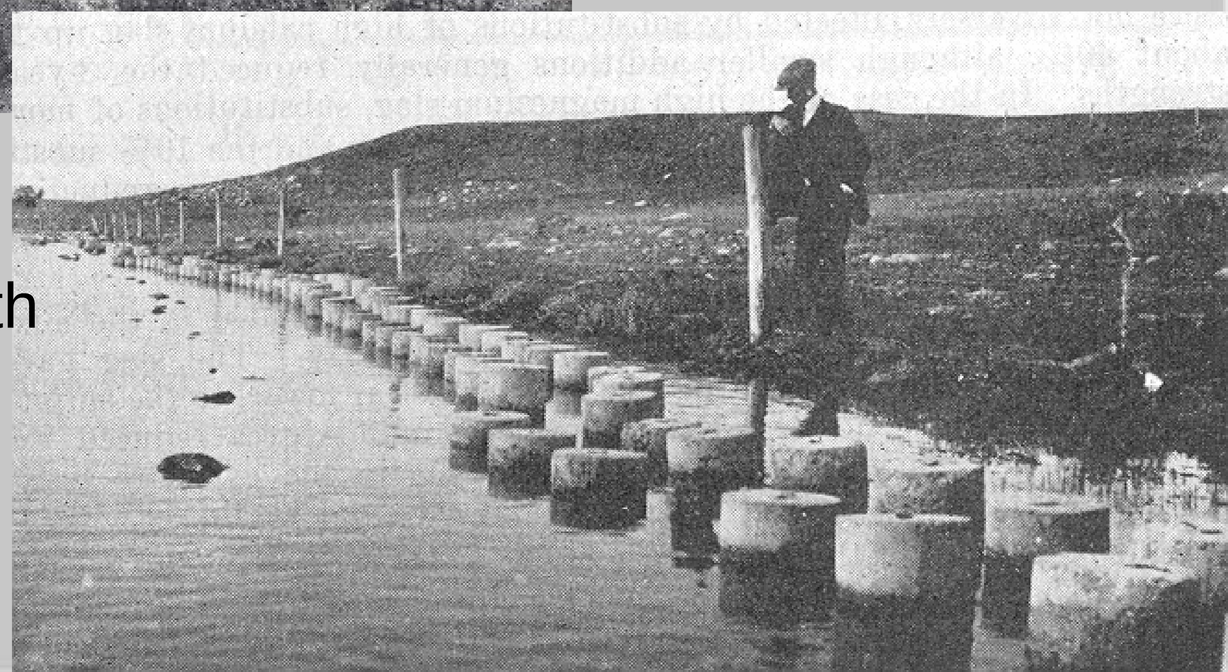
PCA Studies on Sulfate Attack Related to W/C by R. Wilson & A. Cleve, 1921-1928



Montrose, Colorado

2000 cylinders,

10 in. x 24 in. Semi-immersed



Medicine Lake, South Dakota

PCA Studies on Sulfate Attack Related to W/C by R. Wilson & A. Cleve, 1921-1928

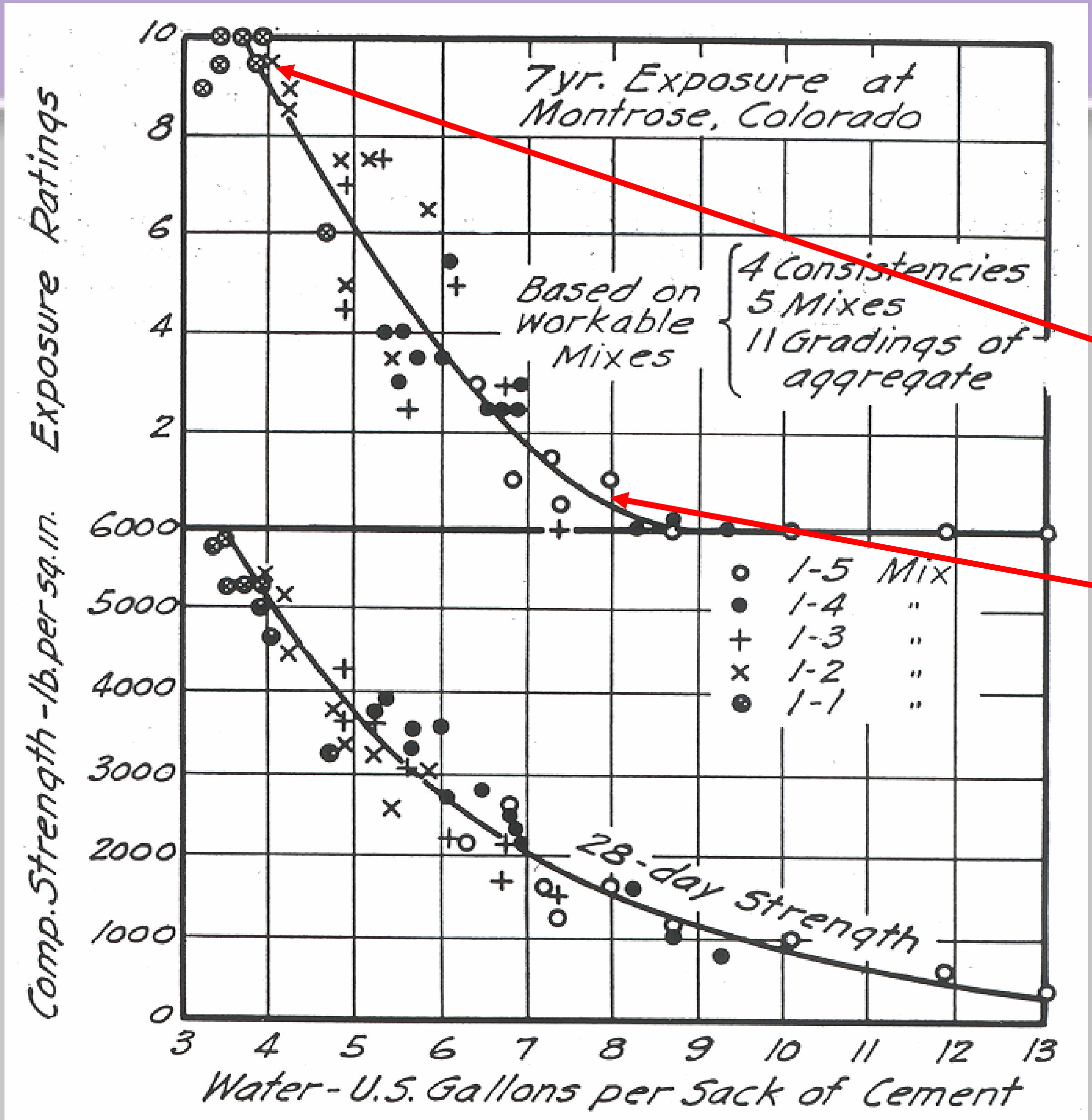


Fig. 3—Water-Cement Ratio Strength and Rating Curves.

Montrose, Colorado

After 7 Years Exposure

4 gal./sack = 0.36 W/C

6 gal./sack = 0.55 W/C

8 gal./sack = 0.73 W/C

Any concrete with W/C > 0.45 was damaged

Standards

- So how do curent North American standards address sulfate resistance?
- And how do they address the various transport mechanisms?

Sulfate Resistance Of Concrete

These issues involve both compositional limits on binder materials, and transport properties

- Limits on C_3A
- Use of Supplementary Cementitious Materials
- Limits on W/CM with implied limits on “Permeability”
- Proper Compaction and Curing
- Air Entrainment

ASTM C 150 Chemical

(Max. %)

Type	I	II	III	V
SO_3 ($C_3A \leq 8$)*	3.0	3.0	3.5	2.3
SO_3 ($C_3A > 8$)*	3.5	N/A	4.5	N/A
C_3A	---	8	15	5**
$C_4AF+2(C_3A)$	---	---	---	25**

*N/A if optimum sulfate test is run and C 1038 expansion is met.

**N/A if optional C 452 sulfate resistance test is run.

Most Type V Cements are never tested for sulfate Resistance!

ASTM C452

- Gypsum is added to mortar bars to get 7.0% SO_3 and 14 day expansion is measured. The test is based on Lerch's results.
- Limits in CSA A5 (0.035% for Type 50) are lower than in ASTM C150 (0.040% for Type V).
- Not suitable for blended cements and SCM's since sulfates are there before these materials hydrate.
- Tests by Hooton indicate that for PC, this test is less conservative than ASTM C1012.

ASTM C 1012 Sulfate Expansion

- Used to test Blended-Cements or Cement+SCM
- Mortar bars are exposed to 5% sodium sulfate solution after attaining 20MPa (3000psi).
- Expansion is measured for 6 or 12 months.
- Limits are specified in ASTM and CSA standards

ASTM C1012

- Developed by K. Mather and ASTM C-1 in 1970's for blended cements and SCM's.
- Mortar bars reach 20 MPa before exposure to 50 g/l Na_2SO_4. This allows SCM's to react before exposure.
- The test is slow (6 to 12 m) since sulfates have to diffuse inwards.
- Specified in ASTM C595, C1157, C989, C1240,
  In CSA A3001, and in ACI 201 (6 to 18 m)

ASTM C1012 Limitations

- Some sulfate salts, e.g., $MgSO_4$, result in reduced pH and acid attack and do not necessarily expand. Therefore, other criteria than expansion may be needed.
- Only uses one (concentrated) sulfate concentration, which may not be the worst case.

- Does not address the issue of wet/dry cycling or evaporative transport of sulfates in arid climates.

pH Controlled Tests

- pH control of small, high-surface area specimens may accelerate attack but is it realistic?

- The pore solutions in concrete have high pH (12-14) and unless exposed to leaching in running water, the pH will likely remain high. Therefore, matching the pH of neutral sulfate salts in laboratory tests maybe irrelevant----but maybe important over 100's or 1000's of years.

Tests for Sulfate Resistance of Cementitious Binder

- Both ASTM C452 and C1012 mortar bar tests only assess the resistance of the cement or binder combination to deleterious expansion associated with the the formation of ettringite.
- In both tests, bars are completely submerged, so diffusion is the only transport process.

Sulfate Resistant Cements

- **Type V cements are *resistant but not immune* to sulfate attack.**
- **In ASTM C1012, Type V cements typically exceed 0.10% expansion in 12 to 24 months and are eventually destroyed.**
- **By comparison, many PC + SCM mixtures have not exceeded 0.10% for much longer periods, up to 20+ years.**

Type V SRPC Performance in C1012 Tests

C_3A	% @ 6 mo	% @ 12 mo	Time to >0.10%
2.0	0.037	0.063	18 mo
2.1	0.032	0.061	18 mo
~2.0	0.052	0.113	11 mo
3.8	0.060	0.273	7 mo
1.4	0.037	0.061	20 mo
Limit	0.050	0.100	-

Not all Type V SRPC's pass the 0.10% at 12 month limit,

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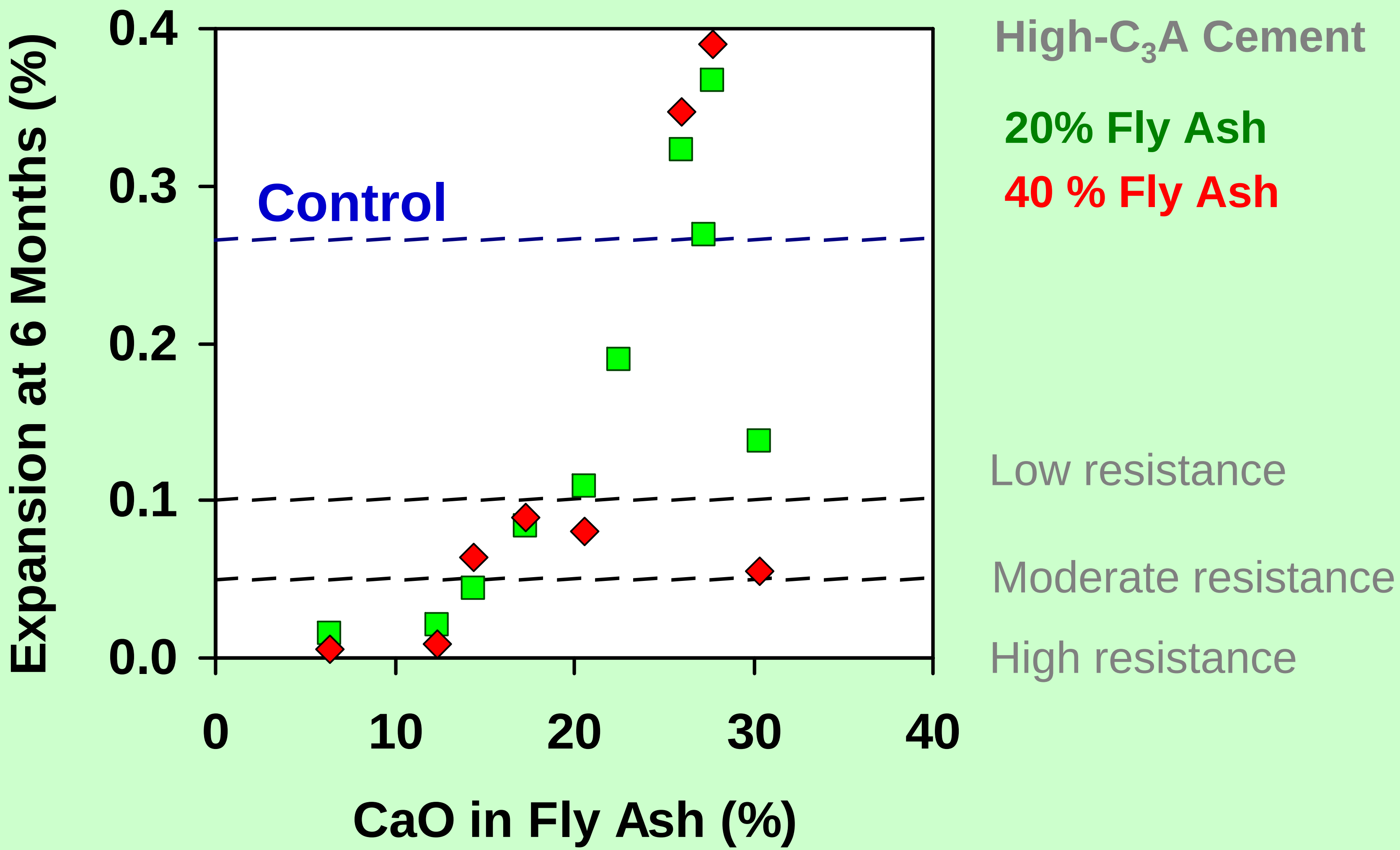
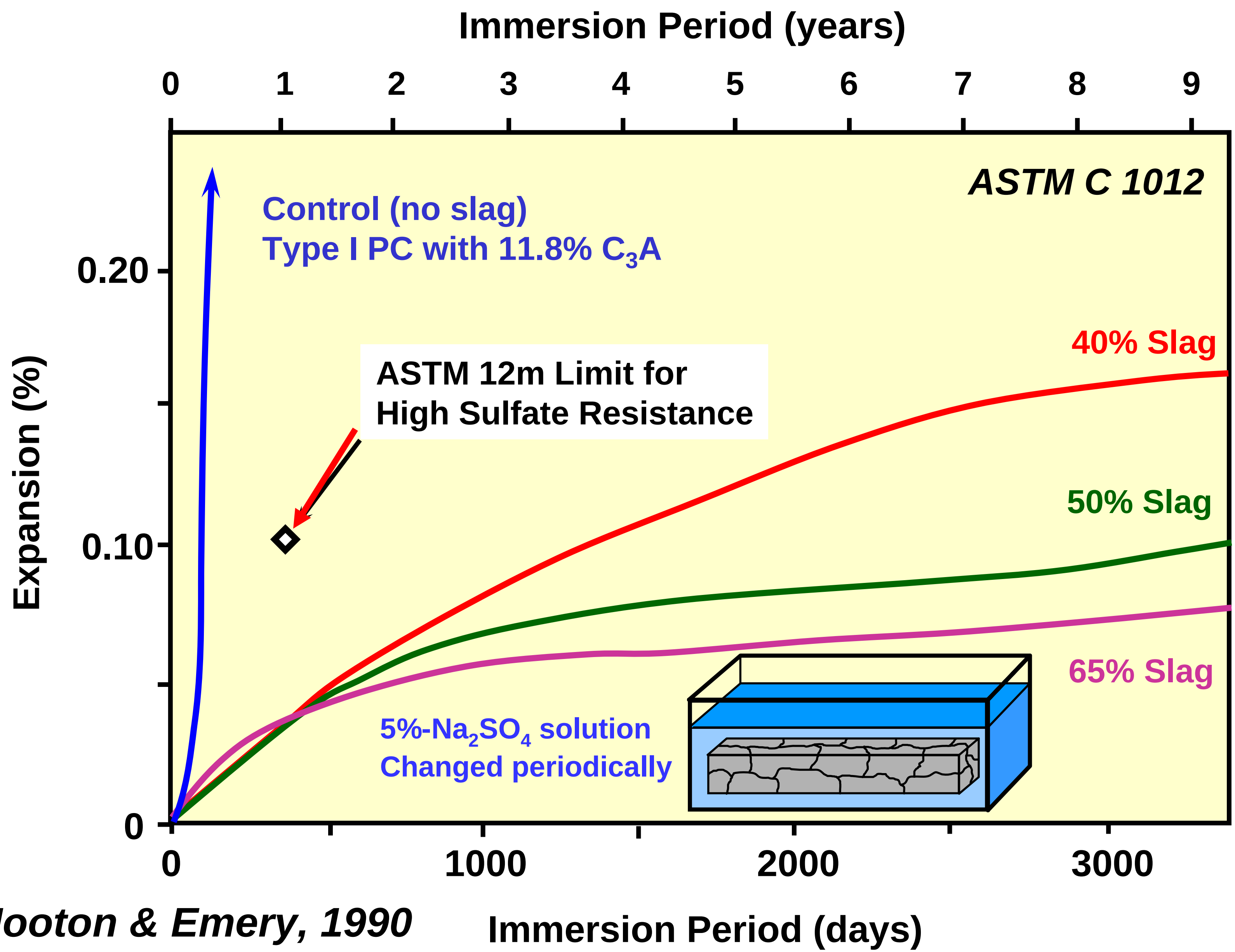
Effect of Fly Ash Composition on Sulfate Resistance



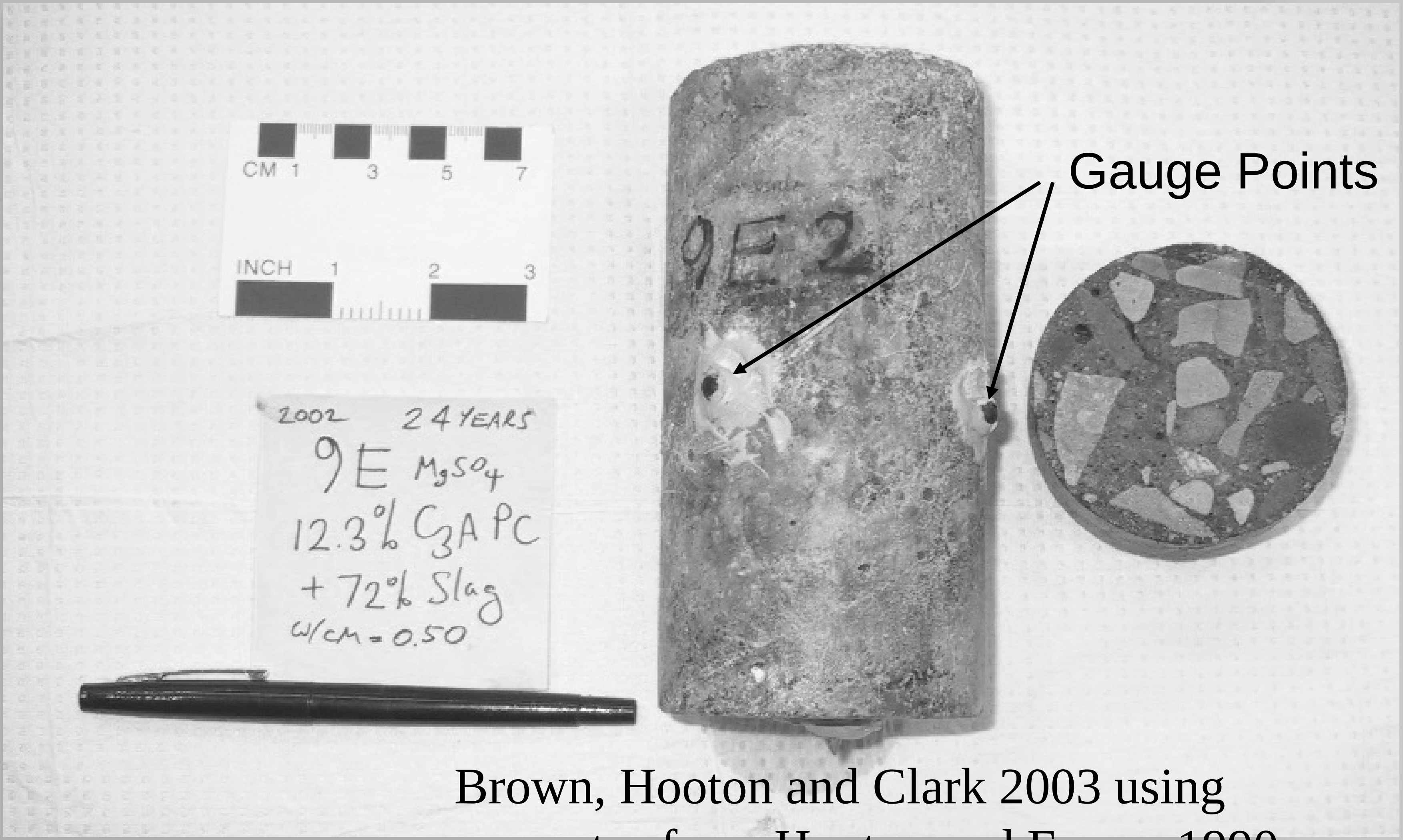
Thomas et al

Effect of Slag on Sulfate Resistance



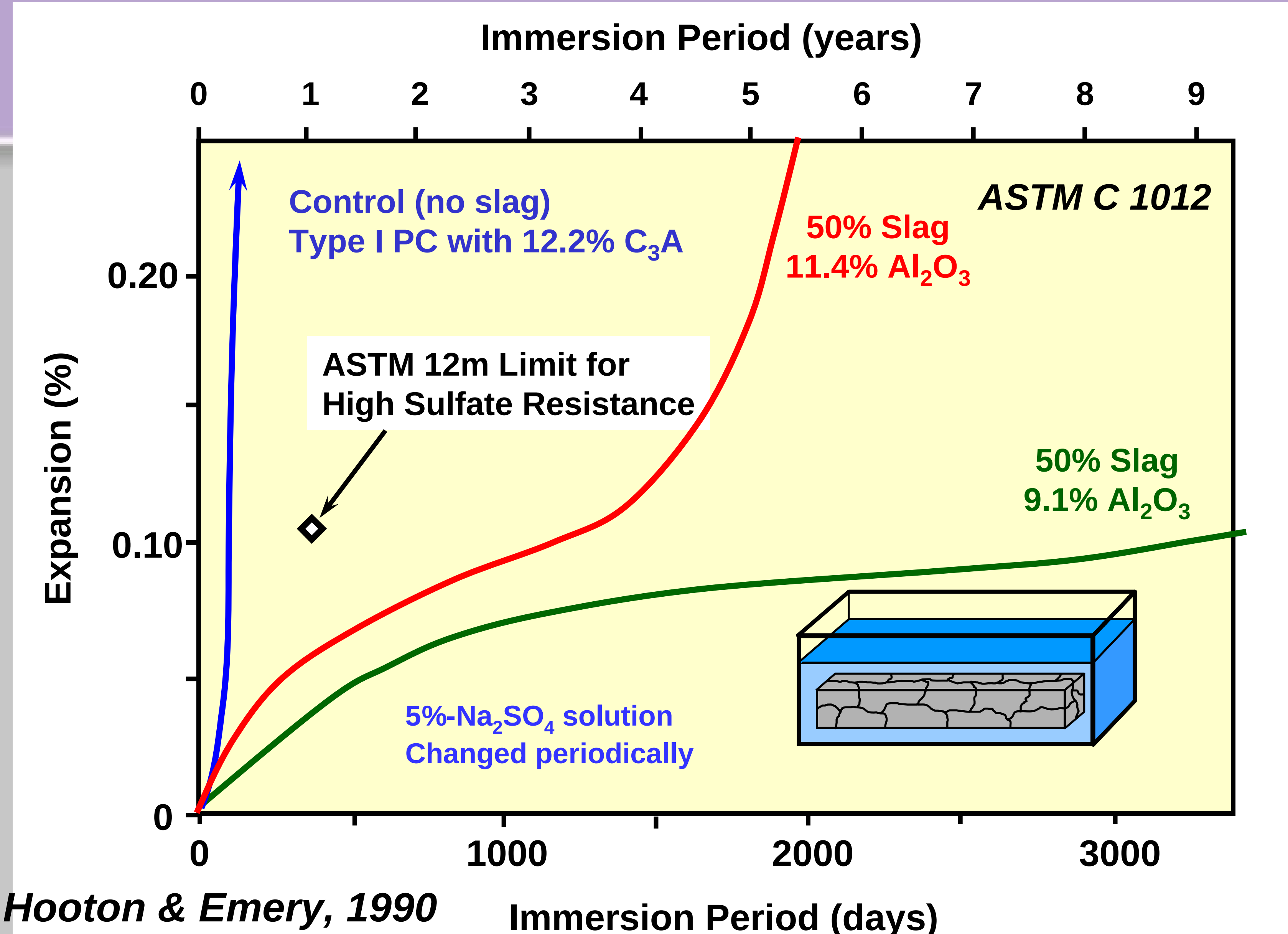
Hooton & Emery, 1990

Type I, 12.3% C_3A Cement + 72% Slag w/c =0.50, in $MgSO_4$ for 24 years: Undamaged



Brown, Hooton and Clark 2003 using concretes from Hooton and Emery 1990

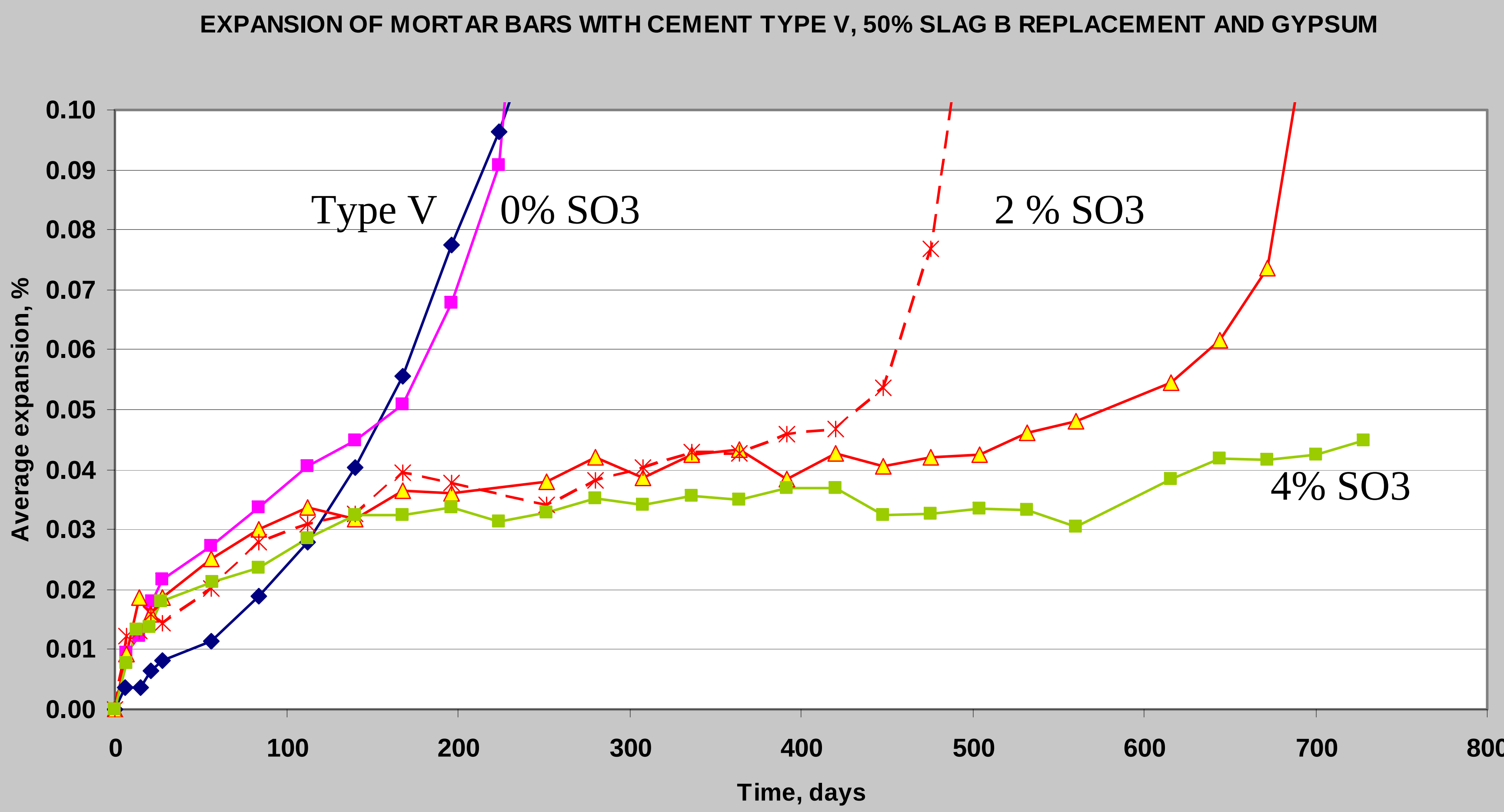
Effect of Slag Al_2O_3 on Sulfate Resistance



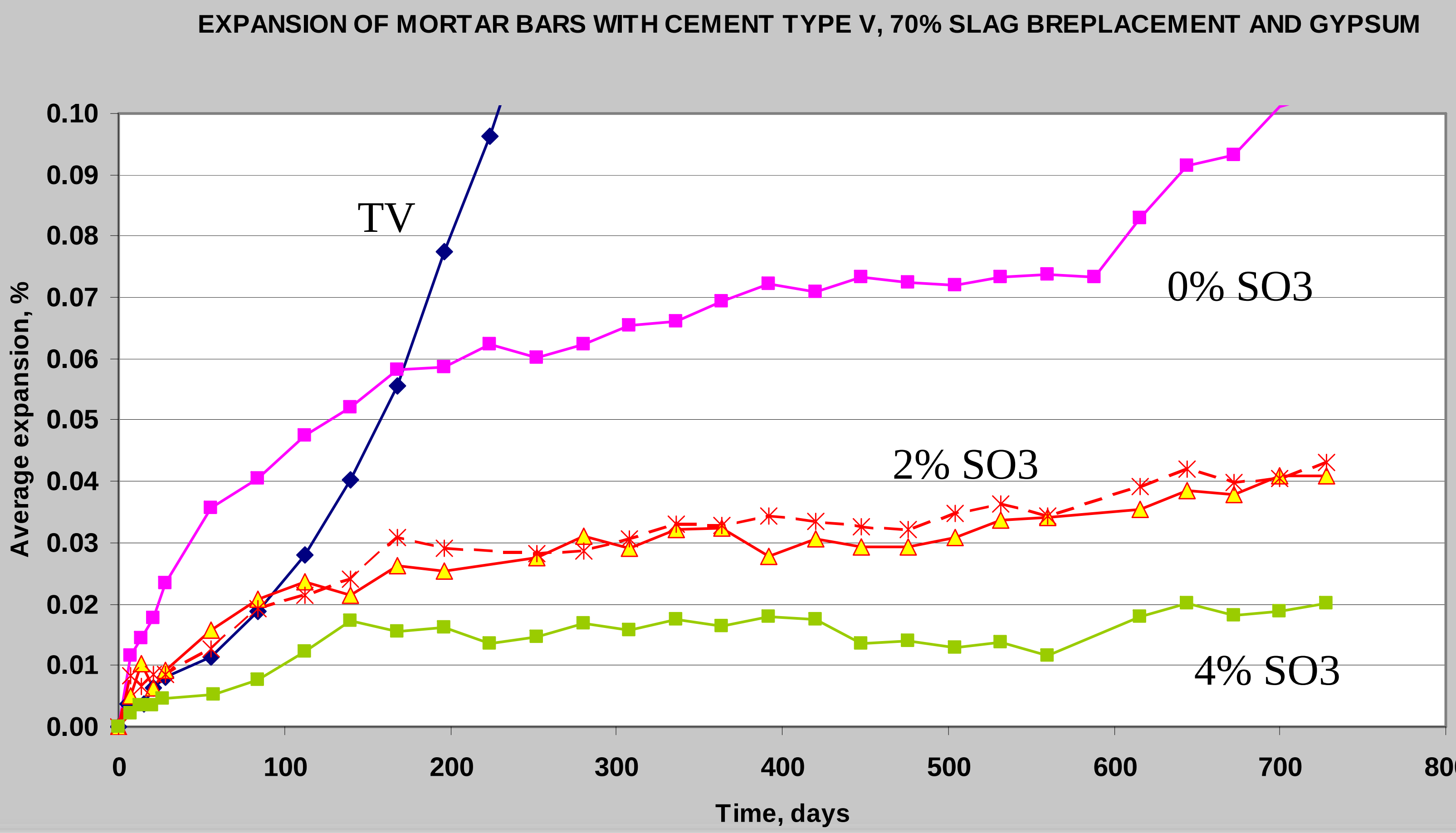
Recent Issues with High-Alumina slag

- While North American slags have low alumina contents (8-11%), many of the offshore slags from the Pacific rim and elsewhere contain high–alumina contents (12-18%).
- These slags provide excellent physical properties and durability in terms of ASR and chloride resistance.
- Their high-alumina contents have raised concerns for sulfate resistant applications, since many of these high-alumina slags do not pass the ASTM C1012 test limits at normal replacement levels (50-70%), especially when tested with some sulfate-resistant Type V cements.

C 1012 Expansion: Type V + 50% of 14.6% Al_2O_3 Slag + Gypsum



C 1012 Expansion: Type V + 70% 14.6% Al_2O_3 Slag + Gypsum



Current Recommendations on High-Alumina Slag Use for Sulfate Resistance

Total alumina levels do not account for all the variable performance. We are currently looking at the available reactive alumina from the slag.

Source-specific materials combinations need to be tested, and tested on an on-going basis.

Concrete Tests?

- There are no standard concrete tests for assessing sulfate resistance.
- The reason is that even in highly concentrated sulfate solutions, the test would take several years to show visual damage, let alone expansion.

Concrete Tests?

As a result of not having a direct concrete performance test, the ACI 318 code uses a 2-pronged approach.

1. The cement binder type is limited by the severity of exposure.
2. Maxima are placed on W/CM depending on the severity of exposure (to limit sulfate ingress).

Concrete Standards

- Both ACI 318 and CSA A23.1 recognize the need for good quality concrete as a defense against sulfate attack. This is done by limiting mix w/cm.

Exposure	ACI	CSA
moderate	0.50	0.50
severe	0.45	0.45
very severe	0.45	0.40

- Use of appropriate cementing materials is secondary to use of impervious concrete for resistance.

ACI C201-2R SULFATE RESISTANCE TABLE

Exposure Severity	SO_4 - Soil %	SO_4 in H_2O ppm	W/CM Max	Cement. Material
Class 0 Negligible	0.00-0.10	0-150	No Req't.	No Req't.
Class 1 Moderate	0.10-0.20	150 to 1,500	0.50	Type II or Equiv.
Class 2 Severe	0.20-2.0	1,500 to 10,000	0.45	Type V or Equiv.
Class 3 Very Severe	2.0 +	10,000 +	0.40	Type V + Pozz/Slag or Equiv.

Equivalence determined using ASTM C 1012 test

ACI C201-2R Equivalence Testing of Cementitious Binders for Sulfate Resistance

Exposure Severity	ASTM C 1012 Exp’n. Limit
Class 0 Negligible	-
Class 1 Moderate	0.10% @ 6months
Class 2 Severe	0.05% @ 6 months, but ok if < 0.10% @ 12 months
Class 3 Very Severe	0.10% @ 18 months

Effect of W/C: USBR 40-Year Data (C_3A from 0 to 8%)

P.J.M. Monteiro, K.E. Kurtis / Cement and Concrete Research 33 (2003) 987–993

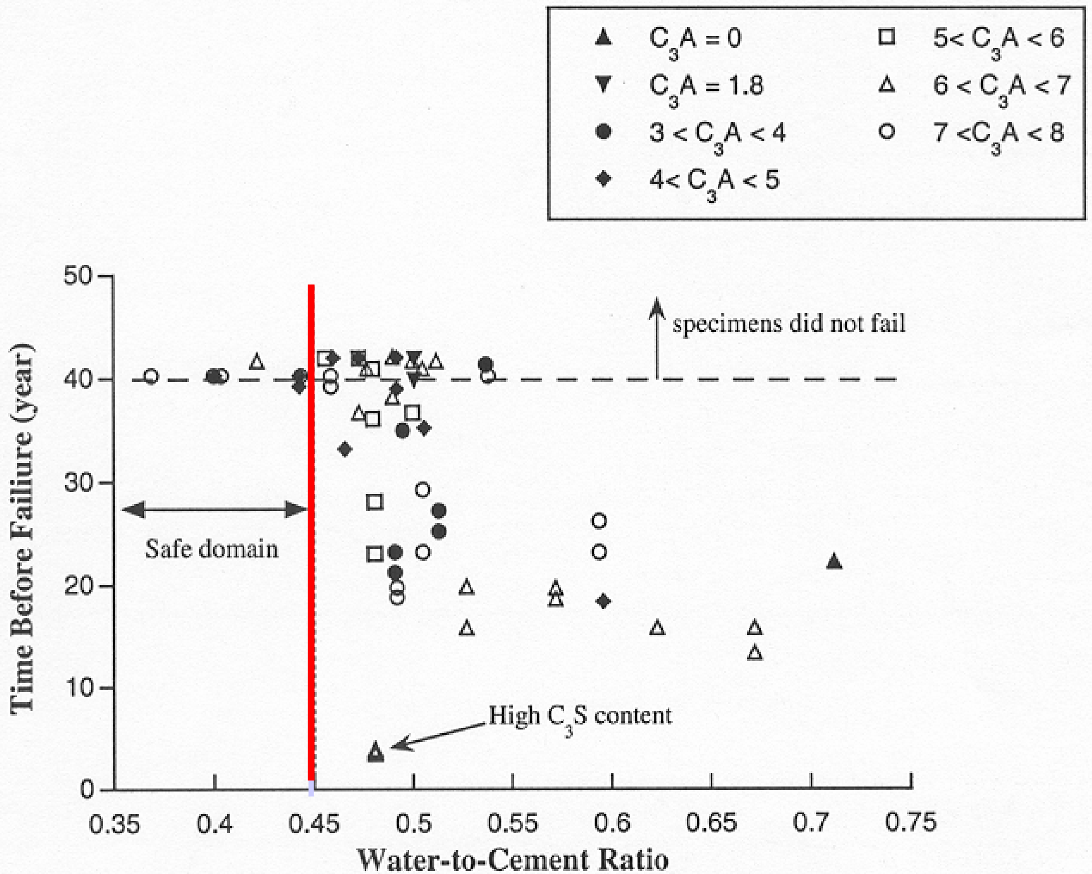


Fig. 2. Time to failure as a function of w/c ratio, with ranges of C_3A content in the range 0–8% shown by the shape and color of the markers.

Concrete in contact with sulfate soil and evaporative transport

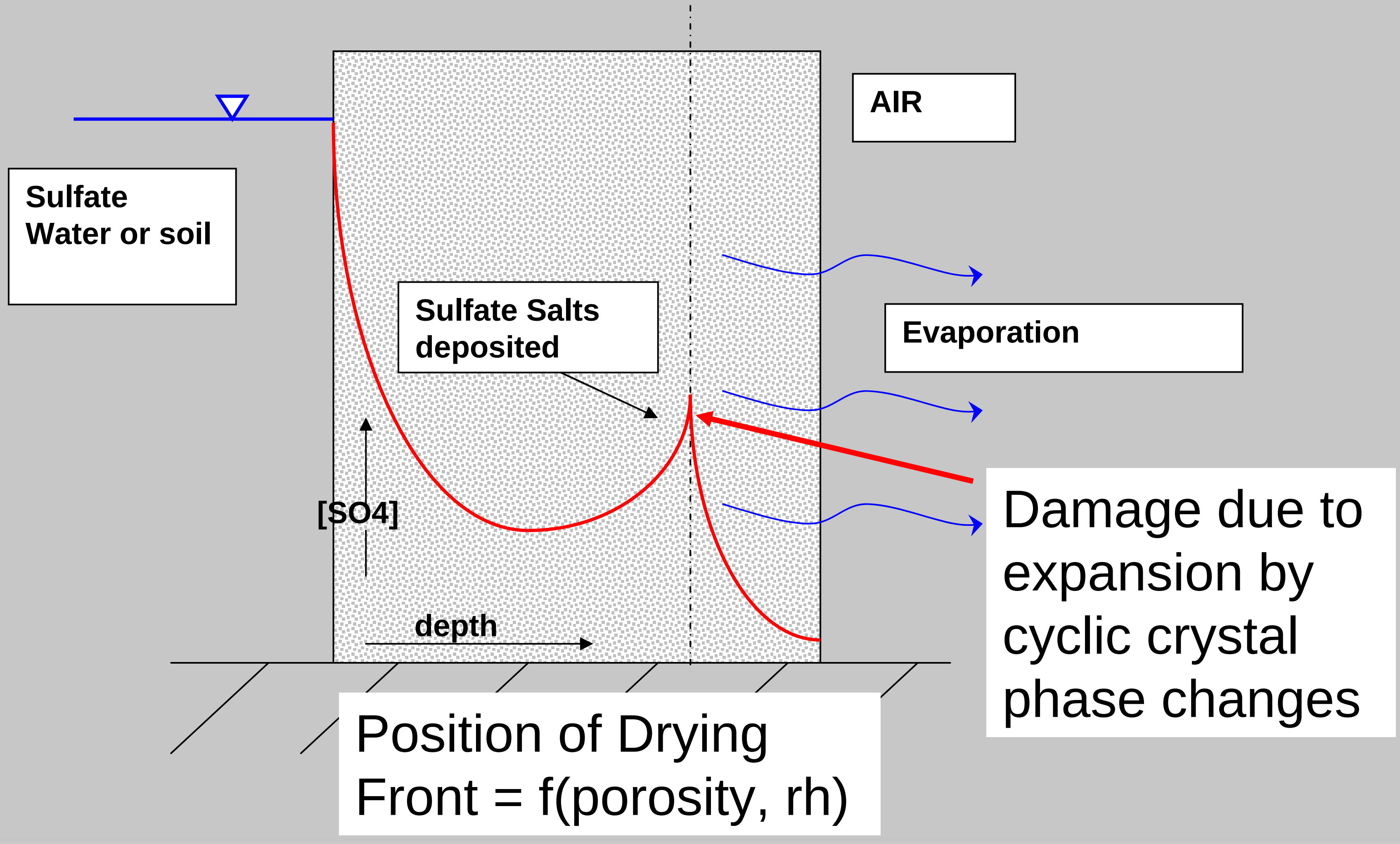
- Visible sulfate attack involves concrete where one part is exposed to evaporation.
- Because of lower relative humidity in Western US and Canada, evaporation is a big issue.
- Sulfate salts are continuously drawn up from the soil and precipitate near the evaporative face to build high concentrations.
- Sulfate salts deposited in pores undergo cyclic crystal phase changes which involve volume increases.
- This results in accelerated concrete disruption.

Sulfate Salt Crystallization

- Current standards deal with evaporative transport and sulfate salt crystallization by limiting the W/CM of concrete.
- At W/CM < 0.45, the rate of evaporative transport rapidly diminishes.

PCA photo

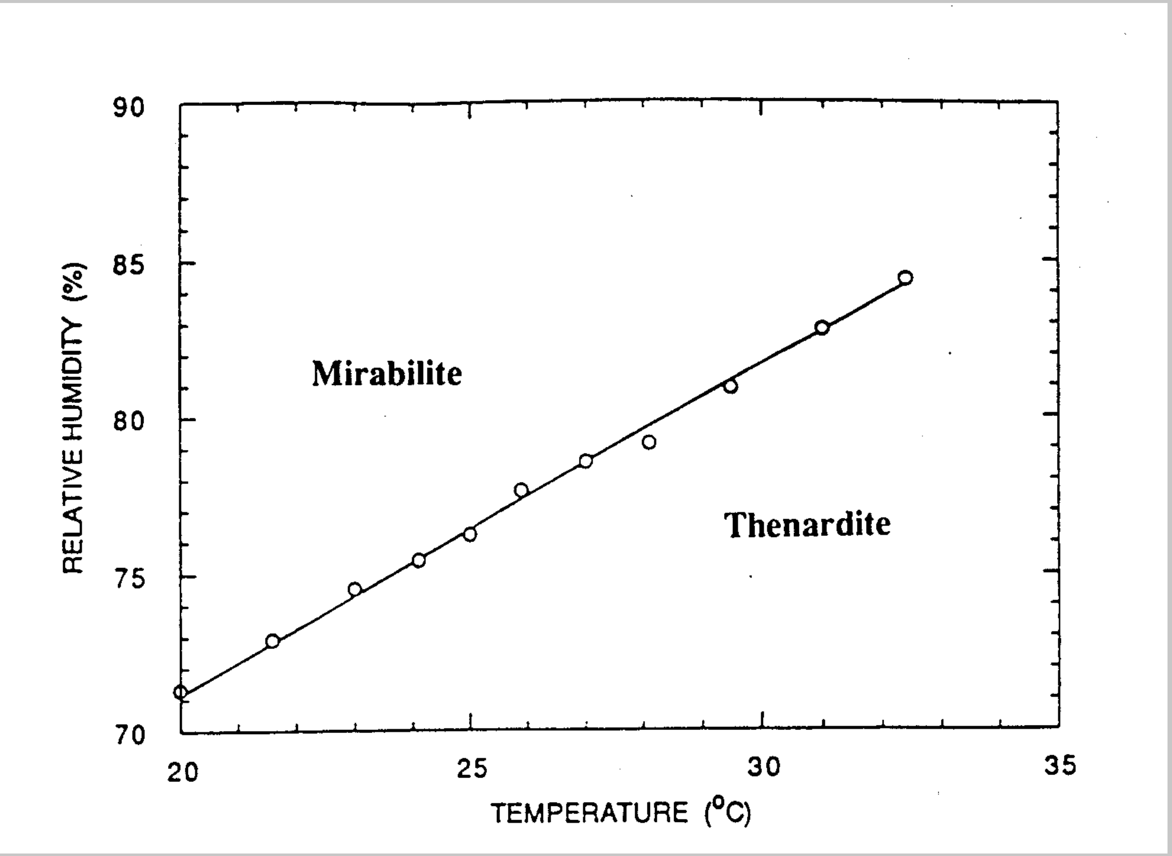
Wick Action


AIR
Sulfate
Water or soil
Sulfate Salts
deposited
Evaporation
[SO4]
depth
Damage due to expansion by cyclic crystal phase changes
Position of Drying Front = f(porosity, rh)

Eg. Phase Changes in Sodium Sulfate

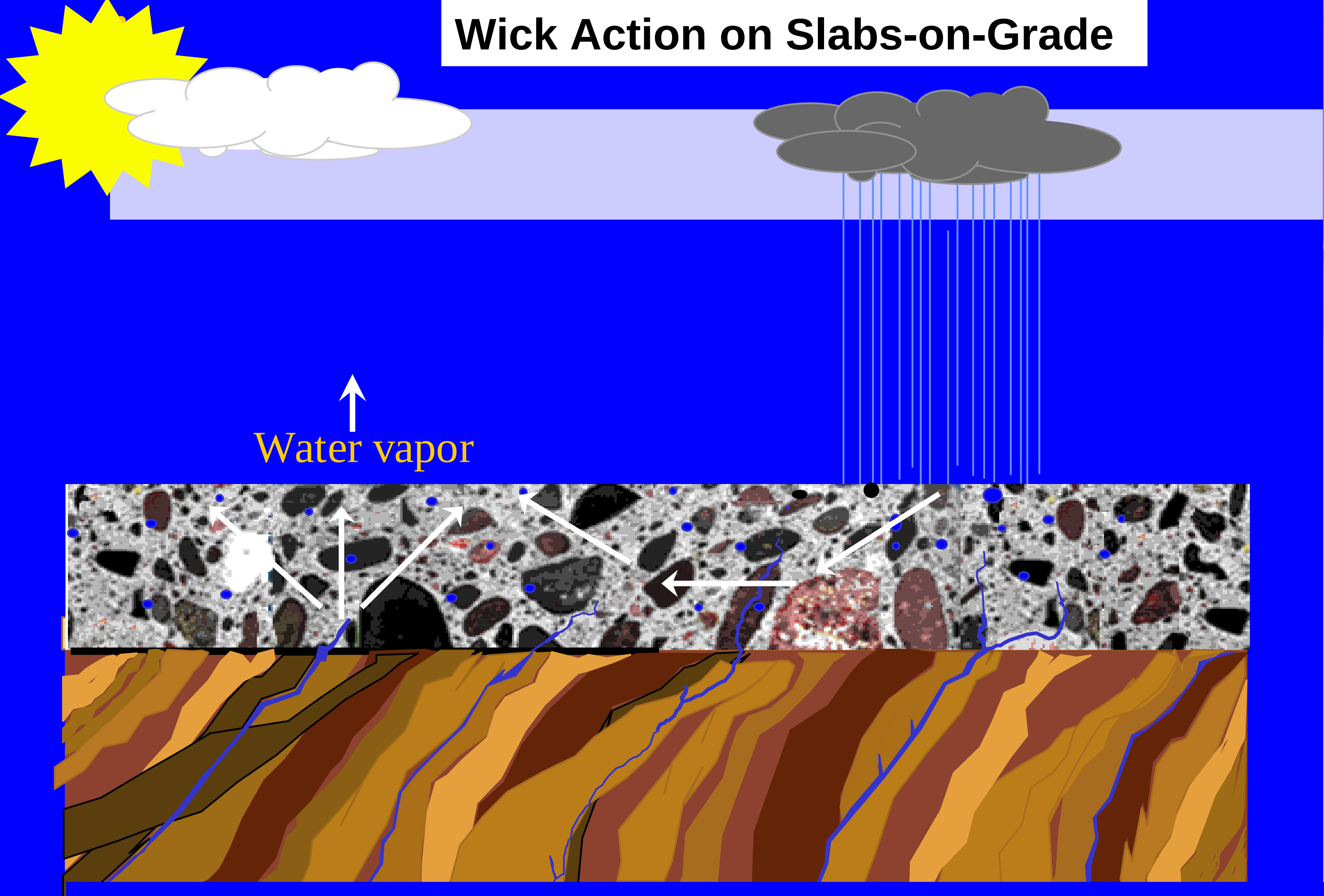
Thenardite $\qquad\qquad$ Mirabilite

$Na_2SO_4 \longleftrightarrow Na_2SO_4 \cdot 2H_2O$



Sandberg & Folliard, 1994

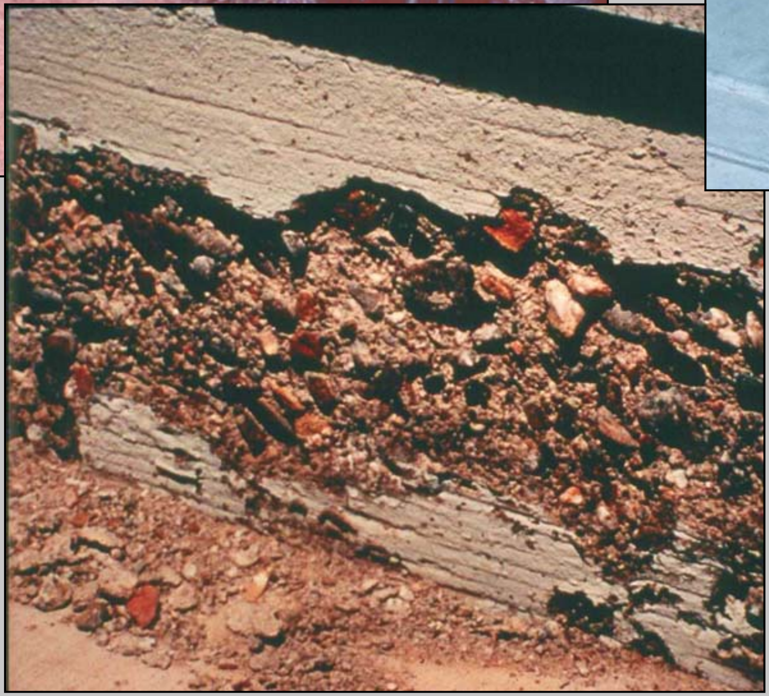
Wick Action on Slabs-on-Grade



Schematic showing moisture movement thru soil & concrete

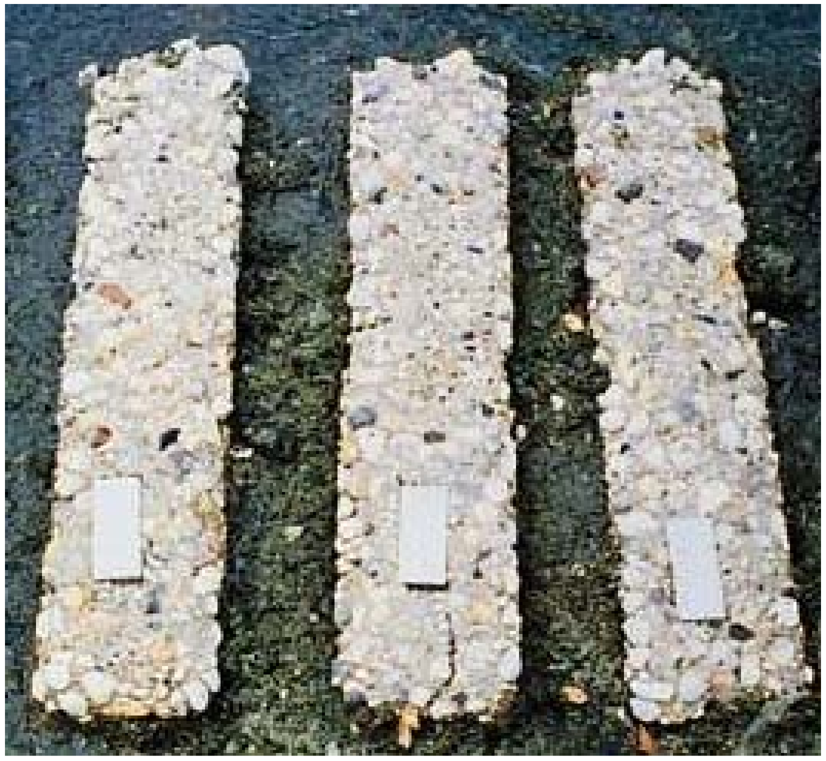
P. W. Brown

Sulfate Salt Crystallization Attack



PCA photos

Effect of W/C Ratio

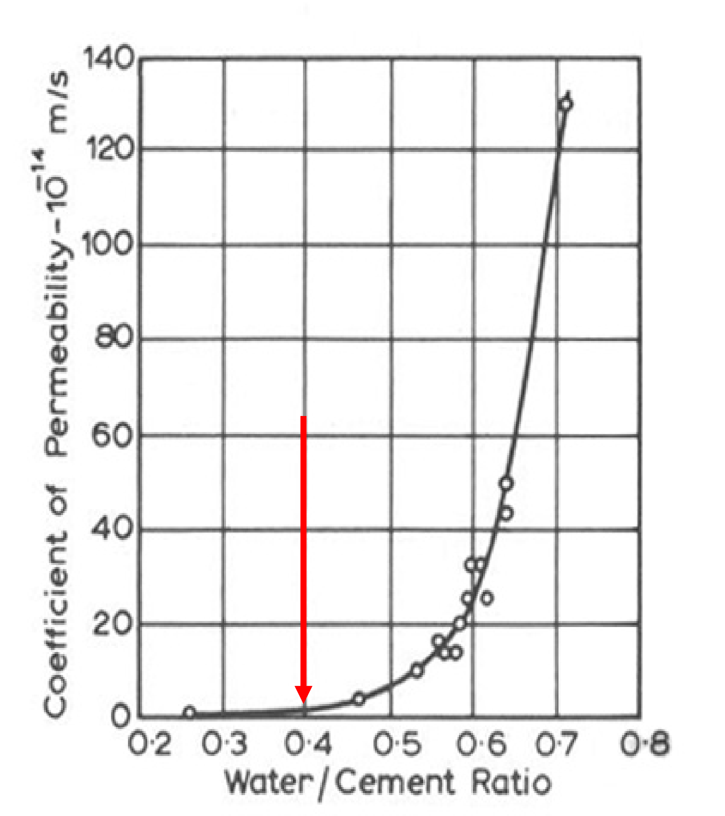


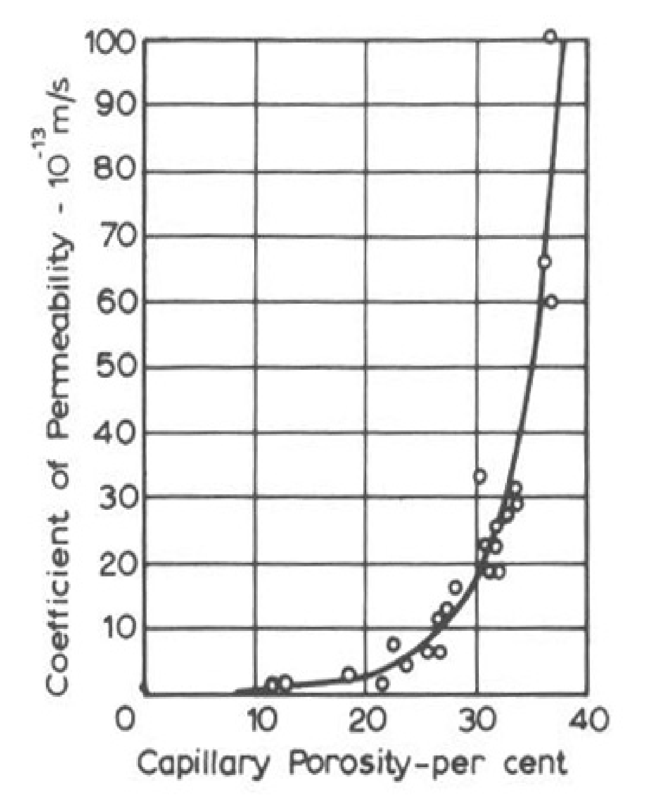
Rating of Concrete: 5 @ 12 yrs
Type V Cement
W/C = 0.65

Rating of Concrete: 2 @ 16 yrs
Type V Cement
W/C = 0.39

PCA, Sacramento Site

The difference is that low w/c, the capillary pore structure is discontinuous





Delayed Ettringite Formation

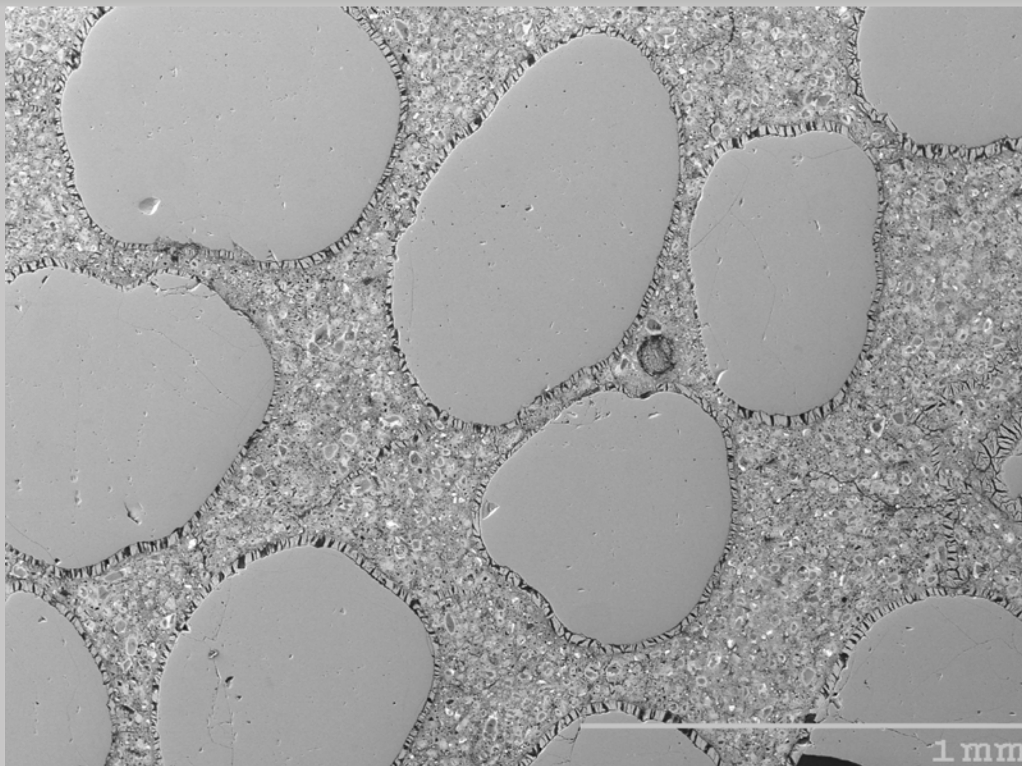
Different from traditional concern with over-sulfated cements, since problems appear to be initiated by high early temperature exposure which makes ettringite unstable. With a source of alkali consumption* and subsequent exposure to moisture, ettringite re-forms and can result in severe cracking.

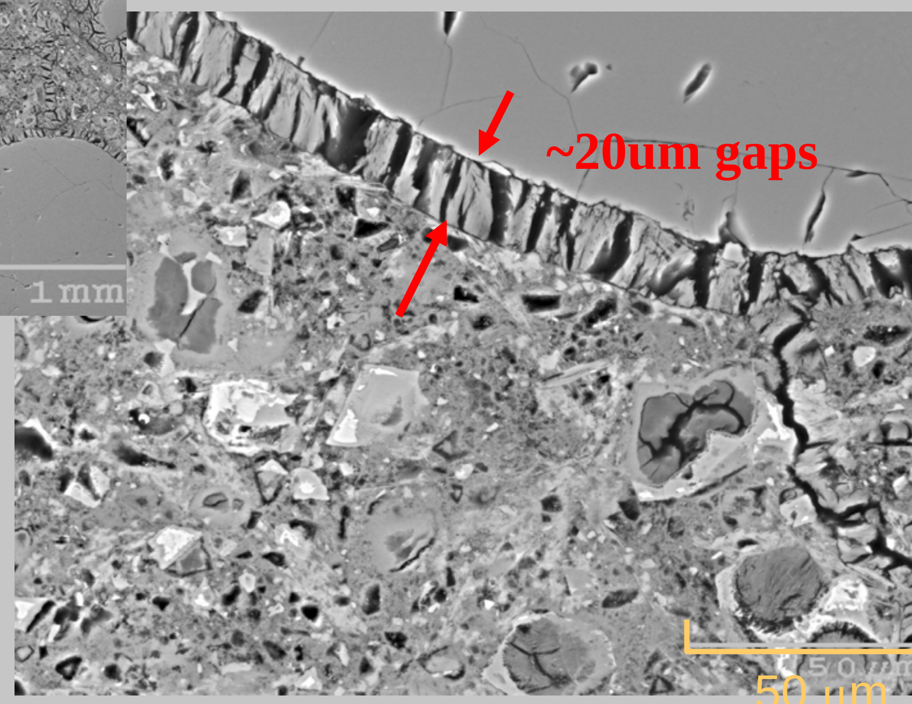
- **Currently, there are no standards except indirectly by controlling max. concrete temp. (eg: CSA A23.4, 65^{o}C).**

  *** Almost all alleged field problems involve ASR aggregates as well, but alkali-leaching can also induce the reaction.**

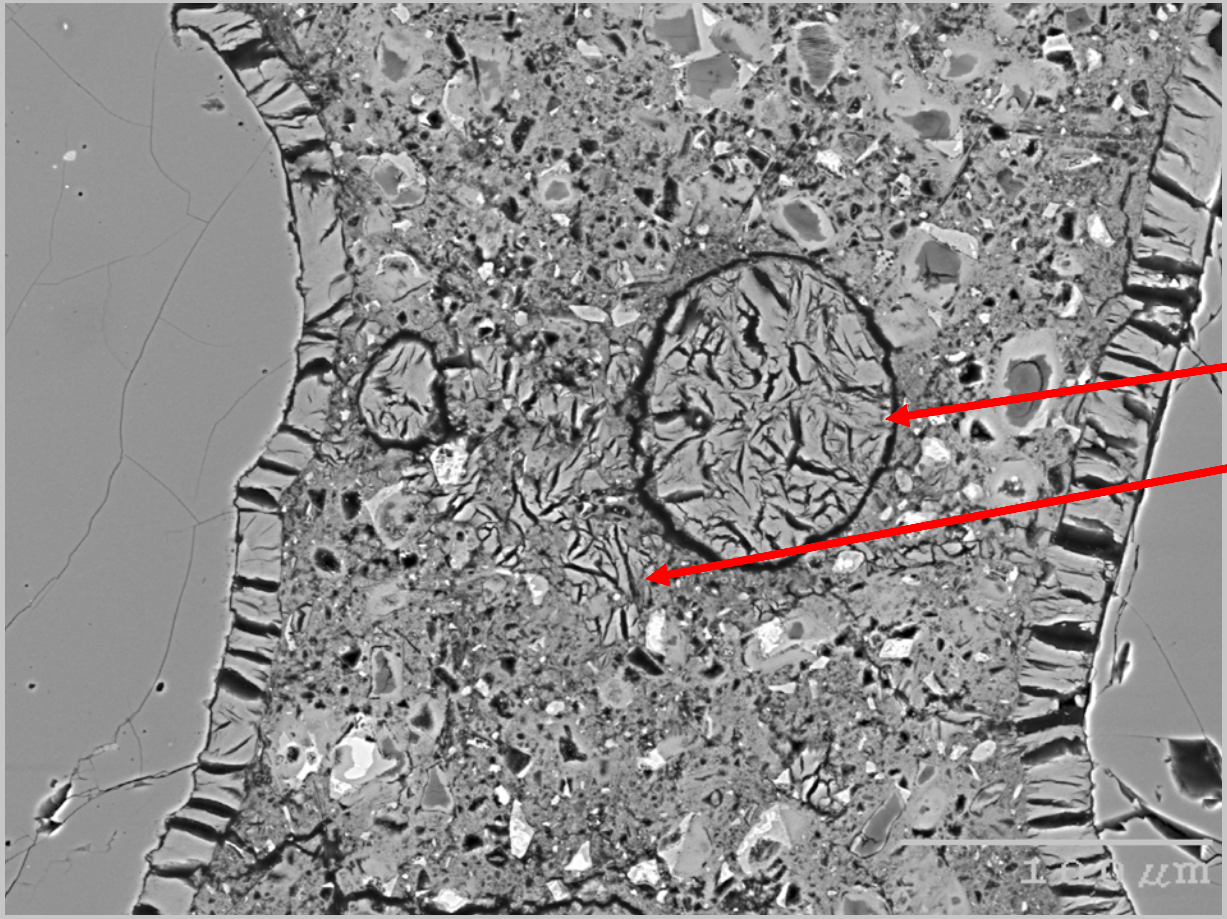
Type III Cured at 95C after 1350 Days

- Ettringite lining expansion rims at paste-aggregate interfaces.
- 2.8% Expansion





Type III PC Cured at 95C after 1350 Days



- **Ettringite lining expansion rims at paste-aggregate interfaces, filling air voids and in porous areas of paste**
- **High Expansion (2.5%)**

Alleged DEF in Texas Foundations

Alleged DEF in concrete box-beam (Texas)

Control of DEF

- Keep heat exotherm below 70C.
- Or Use sufficient pozzolan or slag and keep Temp. <85C

Thaumasite

- A relatively unusual form of sulfate attack usually associated with low temperatures and very wet environments.
- The C-S-H and $Ca(OH)_2$ are converted to gypsum and thaumasite.

$$Ca_6[Si(OH)_6]\cdot(SO_4)_2\cdot(CO_3)_2\cdot24H_2O$$

or: $CaSiO_3\cdot CaCO_3\cdot CaSO_4\cdot 15H2O$

Oxide Compositions of Thaumasite and Ettringite

Thaumasite

$CaSiO_3 \bullet CaCO_3 \bullet CaSO_4 \bullet 15H_2O$

(no alumina)

Ettringite

$Ca_3Al_2O_6 \bullet 3CaSO_4 \bullet 32H_2O$

(no silica)

Consequences of TSA

- Concrete matrix can eventually turn to mush!
- Photo shows a mortar cube that completely converted to thaumasite   at BRE

Recent Case of Excess SO3 leading to TSA

- The thaumasite form of sulphate attack is uncommon, and when it does occur it is typically associated with wet, low-temperature exposures.
- Recently, a concrete producer used a ‘fly ash’ as a partial cement replacement in concrete, where the fly ash was collected from a power plant fueled by petroleum coke and where limestone was injected to scrub the SO2 gases. ---it was mainly anhydrite, with some free lime!

- Concrete structures made with this material hardened but the concrete was weak, and within 6 to 12 months the concrete had expanded and lost most if not all of its structural integrity.
- The sequence of transformations of sulfate phases went from anhydrite to gypsum and ettringite, and then to thaumasite.
- The result was a concrete mush.

Concrete Mixtures

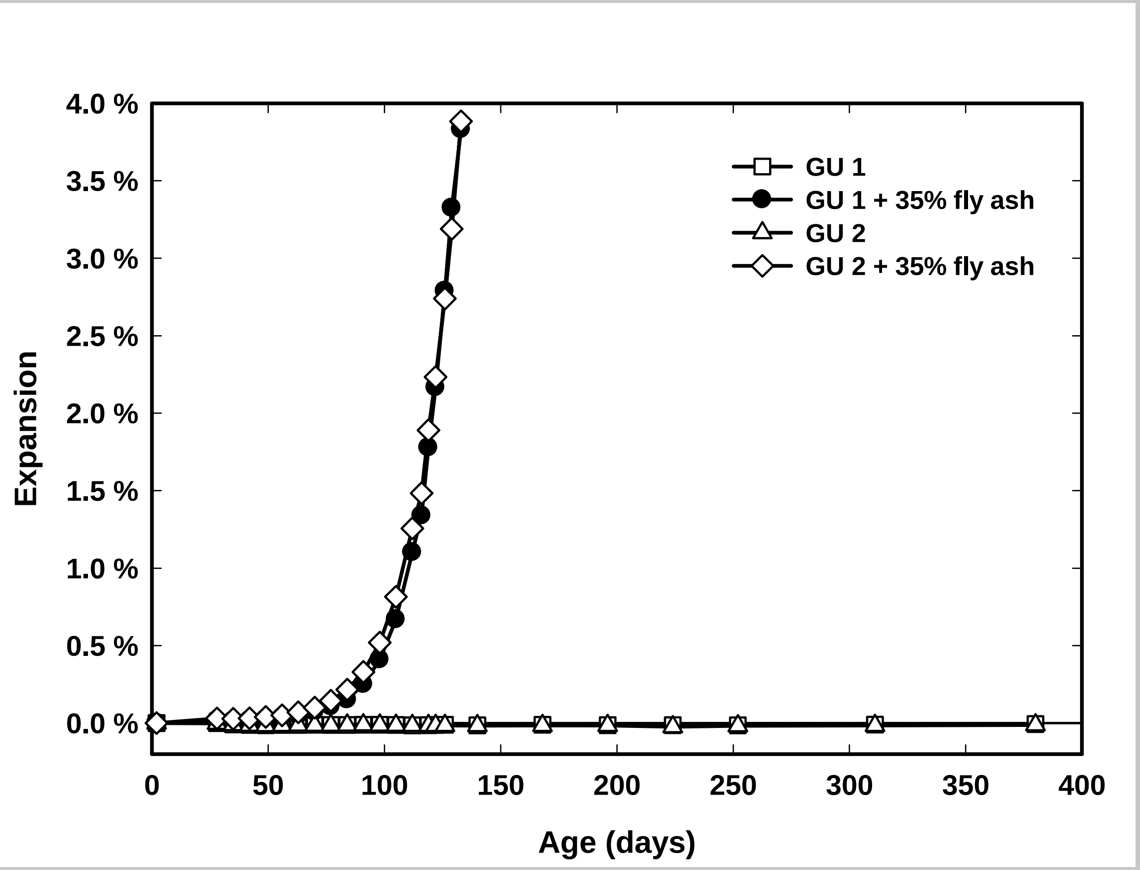
- w/cm= 0.82, CM=196kg/m3 with 0 and 35% “fly ash”.
- 75x75x300mm prisms and 100x 200mm cylinders cast.
- Cured at 23C for 28d, then stored at 5-8C.

Compressive strengths of concrete cylinders

Binder	Compressive strength, MPa					
	7 days	28 days	91 days	115 days	134 days	12 months
GU 1	17.4	22.8	23.8	25.4	25.3	25.6
GU 1 + 35% fly ash	6.6	8.4	7.8	5	1.5	Mush
GU 2	18.9	22.5	23.9	23.7	24.8	24.4
GU 2 + 35% fly ash	5.8	7.6	5.7	1.4	Mush	Mush

Note: Cylinders were moist cured at 23°C to 28 days, then immersed in lime-water at 5-8°C.

Expansions

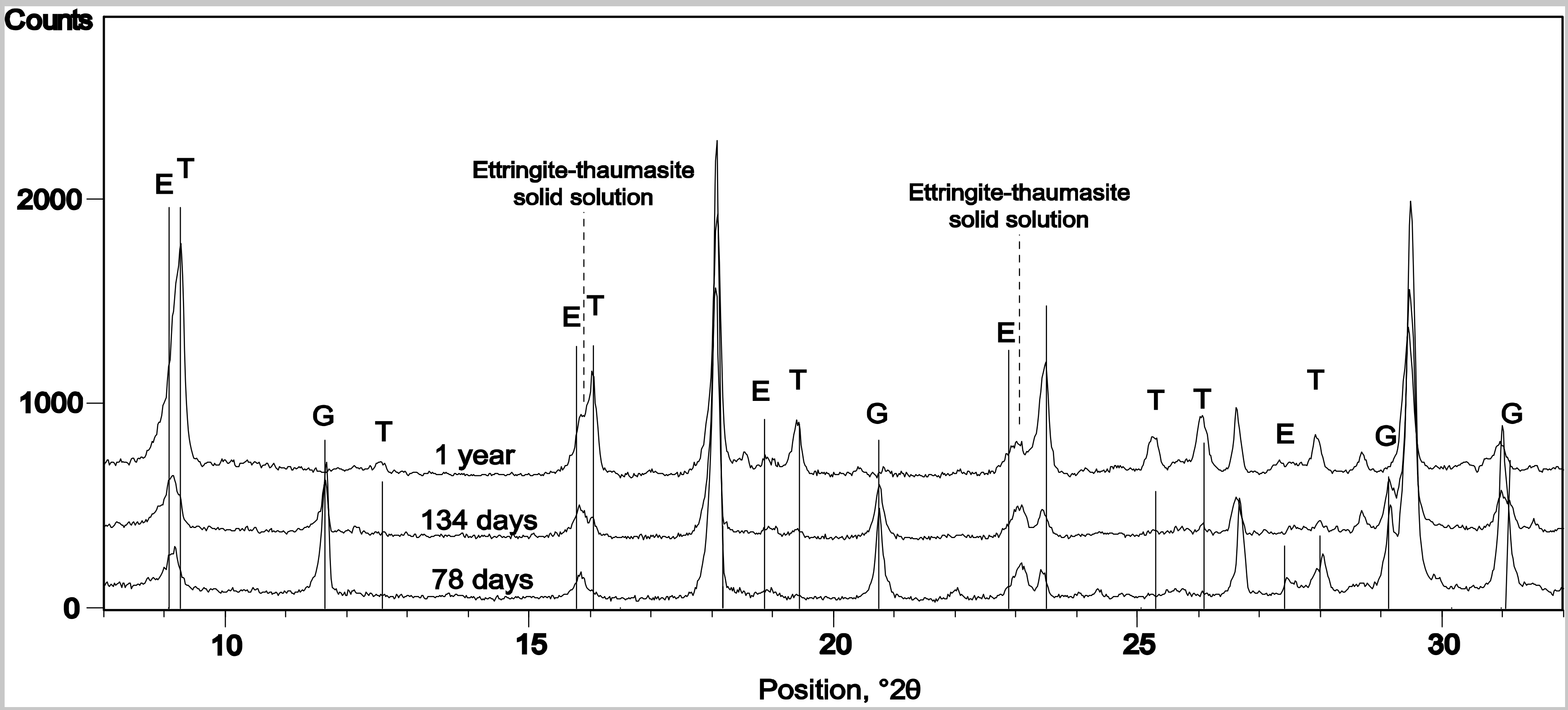


4.0 %
3.5 %
3.0 %
2.5 %
2.0 %
1.5 %
1.0 %
0.5 %
0.0 %
Expansion
0
50
100
150
200
250
300
350
400
Age (days)
GU 1
GU 1 + 35% fly ash
GU 2
GU 2 + 35% fly ash

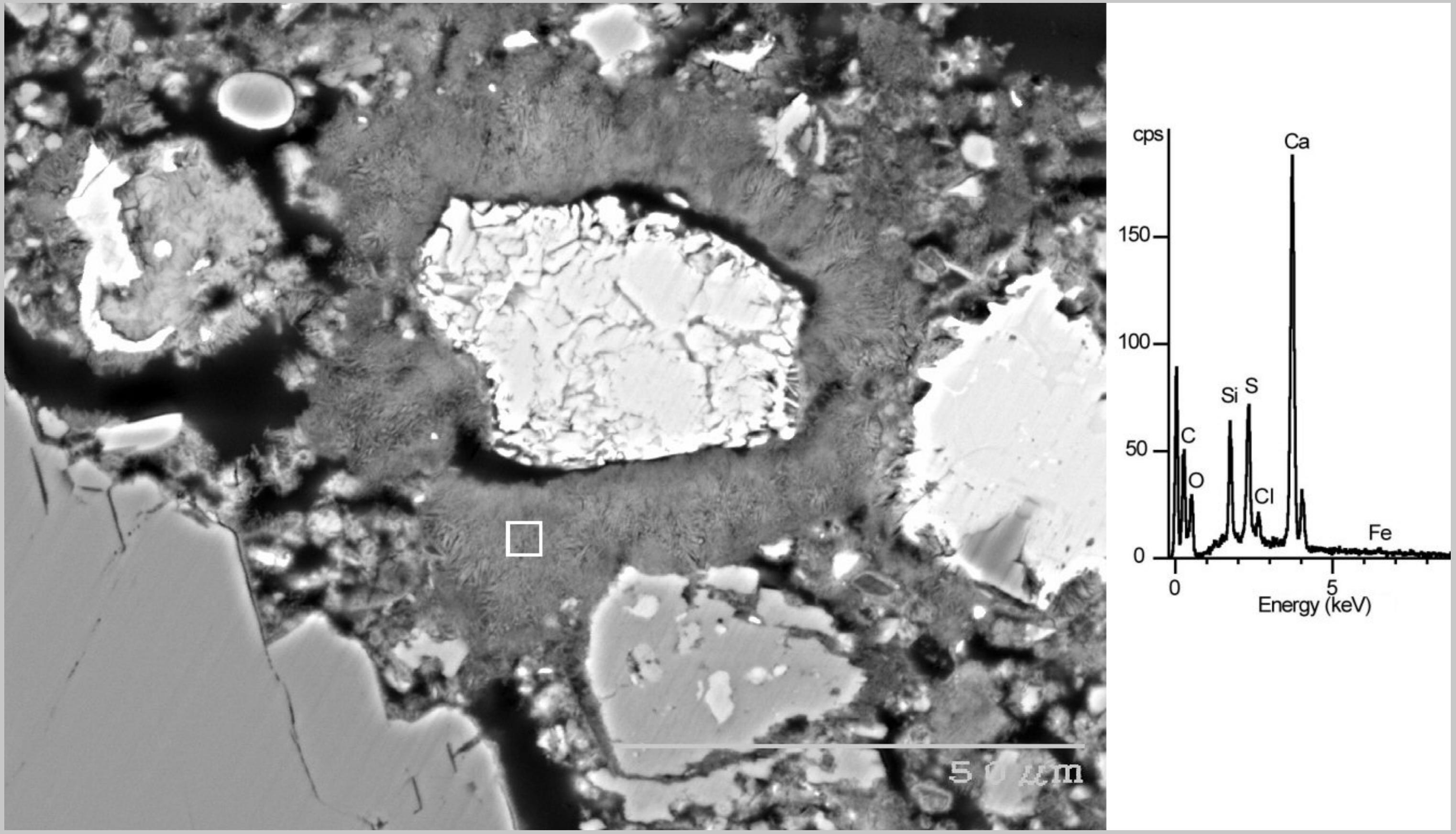
XRD

- An appreciable amount of ettringite (C3A 3C$\underline{S}$ H32) and gypsum were present at 78 days.
- At 134 days some thaumasite (CS C$\underline{S}$ C$\underline{C}$ H15) had formed at the expense of gypsum and strength was much less.
- After 1 year, gypsum was no longer present but the amount of thaumasite had increased and ettringite decreased to 1/5 of T. No residual strength.

XRD of 35% “fly ash” mix with time



BSE Image: 35% fly ash sample at 134 days. EDX is thaumasite



Summary

- For provision of sulfate resistant concrete, the exposure condition needs to be understood as well as the need for good quality concrete.
- Relying solely on cement or binder type is not adequate.
- Standard tests only evaluate the binder and do not mimic all exposures so guidelines for concrete quality (ie. w/c limits or permeability limits) in ACI and CSA need to be followed.
- There is a need to develop guidance to avoid TSA.

For Standards and Codes to be Adequate:

- **The service environment must be understood to know the type of problem to be encountered.**
- **The relevant mechanisms and boundary conditions related to the service environment need to be mimicked by the standard tests or addressed in the codes.**

Or Use the New Scratch and Sniff Test?